Synopsis of the Proposed
Ph.D. Program in Chemistry
on
SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL STUDIES OF SOME SCHIFF BASE METAL COMPLEXES

Submitted to

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SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL STUDIES OF SOME SCHIFF BASE METAL COMPLEXES

Outline of the proposed work /problem

1) Schiff base containing the azomethine (R-CH=N-R) group are condensation products of primary amine with an active carbonyl compound through nucleophilic addition followed by dehydration , under either acid / base catalysis or the existence of heat. Structurally, Schiff base (also known as imine or azomethine) is an analogue of a ketone or aldehyde in which the carbonyl group (>C=O) has been replaced by an imine or azomethine group. An interesting property of transition metal complexes is that they can adopt a wide range of molecular shapes with various coordination modes including linear, tetrahedral, square planar, octahedral structures and other depending on the coordination number of the metal ion and this behavior are unavailable with purely organic compounds.Therefore, in the proposed work we have plan to prepare some new Schiff base ligands derived from substituted hydroxypropiophenone and aromatic or heterocyclic amines and their transition metal complexes. The general formation of Schiff base is shown in following scheme:

2) Transition metal complexes of Schiff bases are studied extensively due to their synthetic flexibility, selectivity as well as sensitivity towards the central metal atom. The imine group (-CH=N-) of Schiff base is a key structural part which is found in various natural compounds of biological significance. A large number of Schiff bases and their complexes have been studied for their interesting and important properties e.g. catalytic activity and transfer of the amine group, photo chromic properties and complexing ability towards some toxic metals. The metal complexes will be prepared by adding the equimolar solution of the ligand in appropriate solvent to the solution of the respective metal salt. A slight excess of the ligand was added to ensure complete precipitation of the metal complexes. The pH of the reaction mixture will be maintained by 1 % KOH solution in methanol to adjust the pH between 7 to 8 and irradiated in Microwave oven for 2-10 min. Progress of the reaction will be monitored by TLC. The solid product obtained was filtered washed and dried in vacuum. The divalent metal ions such as **M = Cu, Cr, Ni, Co, Mn and Zn** will be used in the investigation**.**

Synthesized Schiff bases as well as their metal complexes will be characterized by molar conductance, magnetic susceptibility, electronic spectra, IR, ^{1}HNMR,Mass, spectral studies,

ESR, XRD, TGA, DTA. Metal complexes will also be screened for their antimicrobial and antifungal activities to check their potency.

Introduction:

New Schiff bases derived by the condensation of methyl, chloro, and bromo substituted hydroxy propiophenones with aliphatic and aromatic amines have been synthesized. The Schiff bases are yellow solids with sharp melting points.These Schiff bases were characterized by IR spectroscopy, Nuclear magnetic resonance spectroscopy, UV spectroscopy, and Mass spectroscopy. IR spectra confirmed the presence of the phenolic OH group and azomethine group.

All Schiff's bases having physiological and pharmacological activities associated with exhibiting anticancer, antitubercular and antileprotic drugs used for cure of mycobacterium lepra diseases.
Schiff bases are act as a ligand and they are used in synthesis of co-ordination complexes by treating it with transition metals. These Schiff bases and complexes are characterized by spectral studies. These complexes plays and important role in transition of various ions in vivo. This complex has greater importance because they are taking part in various biological functioning in animals and plants.
Complexes are act as a co-factor in vitamin and proteins. Number of body fluid also has complex structure like hemoglobin and chloroplast.
Complexes also have importance because they are taking part in form framing of structures of animal and plant when they are arranged in polymeric form.

Study of Schiff bases and complexes decide the nature of bonding and structure due to all importance of Schiff bases and their co-ordination complex.

Review of Literature and Development in the subject:-

Schiff base complexes of transition metal have paid great attention in the recent years due to their easy accessibility for synthesis, stability and various biological activities such as antimicrobial, antifungal, antidiabetic, anti-inflammatory, antitumor and antiviral etc. Besides their biological role, several other applications such as catalytic, corrosion inhibition effect, industrial and electronic applications further enhance their importance. This may be due to the presence of azomethine (>C = N -) linkage, which coordinate to the transition metals very easily showing notable antimicrobial and antifungal activities as compare to parent ligands hence very vast literatures is available.

Schiff bases are condensation products of primary amines with carbonyl compounds and were first reported by scientist Schiff [1] in 1864. The common structural feature of these compounds is the azomethine group with a general formula RHC=N-R^1, where R and R^1 are alkyl, aryl, cyclo alkyl or heterocyclic groups which may be variously substituted. These compounds are also known as anils or imines. Several studies [2-5] showed that the presence of a lone pair of electrons in a sp^2 hybridized orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance. Because of the relative easiness of preparation, synthetic flexibility, and the special property of >C=N group, Schiff bases act as excellent chelating agents [6-12] especially when a functional group like –OH or –SH is present close to the azomethine group so as to form a five or six member ring with the metal ion.

Versatility of Schiff base ligands and biological, analytical and industrial applications of their complexes attracted us for further investigations in this area.

Nowadays, the research field dealing with Schiff base coordination chemistry has expanded enormously. The importance of Schiff base complexes for bioinorganic chemistry, biomedical applications, supra molecular chemistry, catalysis and material science, separation and encapsulation processes, and formation of compounds with unusual properties and structures has been well recognized and reviewed. Schiff bases resulted from aromatic aldehydes *ortho-substituted* with a hydroxyl group have initially arouse the researchers' interest because of their ability to act as bidentate ligands for transitional metal ions [13-20]. Later, in studies concerning quantitative structure-antitumor activity relationship of a series of Schiff bases derived from variously substituted aromatic amines and aldehydes, it has been shown that azomethines from salicylaldehydes gave the best correlation [21, 22]. Schiff bases of salicylaldehydes have also been

reported as plant growth regulators [23] and antimicrobial [24] or antimycotic [25] activity. Schiff bases also show some analytical applications [26]. Schiff Bases are characterized by the -N=CH- (imine) group which imports in elucidating the mechanism of transamination and rasemination reaction in biological system [27-29].

Schiff bases are active against a wide range of organisms for example; *Candida Albicans, Escherichia coli Staphylococcus aureus, Bacillus polymxa, Trychophyton gypseum, Mycobacteria, Erysiphe graminis* and *Plasmopora viticola*.

A large number of different Schiff base ligands have been used as cation carriers in potentiometric sensors as they have shown excellent selectivity, sensitivity, and stability for specific metal ions such as Ag(II), Al(III), Co(II), Cu(II), Gd(III), Hg(II), Ni(II), Pb(II), Y(III), and Zn(II) [30-36]. Schiff bases have been studied for their important properties in catalysis [37]. They show catalytic activity in hydrogenation of olefins [38]. They find applications in biomimetic catalytic reactions.

An interesting application of Schiff bases is their use as an effective corrosion inhibitor, which is based on their ability to spontaneously form a monolayer on the surface to be protected. Many commercial inhibitors include aldehydes or amines, but presumably due to the C=N bond the Schiff bases function more efficiently in many cases [39]. The principal interaction between the inhibitor and the metal surface is chemisorption [40]. The inhibitor molecule should have centers capable of forming bonds with the metal surface by electron transfer. In such cases the metal acts as an electrophile and the inhibitor acts as a Lewis base. Nucleophilic centers, such as oxygen and nitrogen atoms, of the protective compound have free electron pairs which are readily available for sharing together with the atoms of the benzene rings they create multiple absorption sites for the inhibitor thus enabling stable monolayer formation [41].

Imines also have biological importance. An imine linkage between the aldehyde derived from vitamin A and the protein opsin in the retina of the eye plays an important role in the chemistry of vision. Vitamins are also called coenzymes, meaning that they are to the functioning of many enzymes, which are large proteins that catalyze chemical changes in cell. An example of a biologically important aldehyde is *pyridoxal phosphate*, which is the active form of the vitamin B_6. Vitamin B_6 serves as a coenzyme by forming an imine with an amino acid grouping an enzyme. The coenzyme, bound to the enzyme, is involved in transamination reaction, the transfer of the amino group from one amino acid to another, which is important in

the metabolism and the biosynthesis of amino acids. In the last step, enzyme-catalyzed hydrolysis cleaves the imine to pyridoxal and the modified amino acid.

Schiff bases have been reported for various biological properties, such as, antibacterial, antifungal activities [42-45]. Metal complexes of them have been widely studied for anticancer and herbicidal applications [46, 47]. They serve as models for biologically important species. *O-phenylenediamine* Schiff bases show clinical properties [48]. Isatin Schiff bases were reported to possess antiviral, anti-HIV, antiprotozoal and anthelmintic activities [49]. They also exhibit significant anticonvulsant activity, apart from other pharmacological properties [50]. Certain cobalt Schiff base complexes are reported as potent antiviral agents [51]. Schiff bases derived from 4-dimethylamine benzaldehyde shows antibacterial activity. In medicines used as antibodies and anti-inflammatory agents [52-56]

PREVIOUS WORK:

1) POTENTIOMETRIC STUDIES OF Cu(II) COMPLEXES WITH SOME SCHIFF BASES

The present paper represents the systematic solution study of complex formation of Cu (II) ion with Schiff bases synthesized from substituted hydroxybenzaldehyde- L1 = {4-[(3, 5-diiodo-2-hydroxyphenyl)methylidine]amino}-1, 5-dimethyl-2-phenyl-1, 2-dihydro-3H-pyrazolone; L2 = {4-[(2- hydroxyphenyl) methylidine]amino}-1, 5-dimethyl-2-phenyl-1, 2-dihydro-3H-pyrazol-3-one and L3 = {4- [(5-iodo-2-hydroxy-3-nitrophenyl)methylidine]amino}-1,5-dimethyl-2-phenyl-1, 2-dihydro-3H-pyrazol-3- one have been studied at 30 ± 0.10C and 0.1 M ionic strength in 60% (v/v) ethanol-water medium. The stability constant of these complexes indicates the formation of 1 : 1 and 1 : 2 complexes with all the Schiff bases.

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2) pH METRIC STUDY OF BINARY AND TERNARY COMPLEXES OF CU (II) WITH PROPIOPHENONE DERIVATIVES AND AMINO ACIDS.

Proton ligand and Metal ligand formation constant of ternary complexes of the type MLB [Where L = i) L1= 3-chloro,2-hydroxypropiophenone (3-Cl- 2HP) ii) L2 = 2-hydroxypropiophenone (2-HP)] and B = [B1= Hippuric(hip) acid, B2= Glutamic acid (glu) B3=Histidine (hist), B4=Aspartic acid (Asp)] And M = Cu (II) have been determined by potentiometrically in biologically relevant conditions at ionic strength ì = 0.1M NaClO4 the overall stability constant have been evaluated using SCOGS computer program. The complexation equilibria have been derived on the basis of concentration species distribution curve and percentage distribution curve. In all cases primary ligands and secondary ligands are found to be compatible ligands. And there by proving greater stability of ternary complexes as compared to binary ones. The stability of ternary complexes expressed in terms of thermodynamic parameter ï log k. and Negative values of ï log k suggest that, the formations of ternary complexes are favorable. And the order of stability constant of ternary system with amino acids for respective primary ligands is. L1= B3> B4 > B2 >B1and L2= B3> B4 > B2> B1.

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Objectives of Research:

Aims and Objectives

The Schiff bases are widely studied ligands, in their neutral or deprotonated forms, to form stable complexes with most of the transition and non-transition metal ions. Tridentate and tetradentate Schiff bases are of particular interest not only for existing them in *keto-enol* forms and can coordinate in neutral, monoanionic, dianionic or trianionic forms but they also offer a variety of bonding possibilities in metal complexes which have even coordination number of six or seven. Furthermore, Schiff base propiophenone bearing nitrogen containing moiety have attracted considerable attention due to their impressive chemical and analytical applications as selective metal extracting agent as well as in spectroscopic determination of certain transition metals Schiff base metal complexes have interesting application in biology, agriculture, medicinal, engineering and catalytic reactions. Due to the great significance in various fields, there is a great excitement in the synthesis of new Schiff bases and their metal complexes. Therefore, it becomes highly significant to synthesis few complexes with new Schiff bases and to investigate their physiochemical properties and utilize them as antimicrobial drugs.

The Schiff bases and their transition metal complexes have found paramount applications in various fields such as food, dyes, biology, agriculture, polymer science, catalysis, analytical chemistry and medical science. The synthesis of numerous newer organic chelating agents particularly Schiff base ligands that can co-ordinate with transition metal ions has created much interest among the researchers working in this field. Since transition metals form stable complexes with Schiff base ligands, the research scientists working in this field have ventured into the study of these complexes with the help of modern physicochemical techniques. Schiff base complexes shows wide range of antimicrobial and antifungal activities against various bacteria and fungi and the enhanced activities are associated with Schiff base metal complexes due to presence of azomethine (>C = N -) groups in their skeleton.

Objectives of the proposed work

The proposed studies will comprises of the following sequential steps to access the proposed objectives:

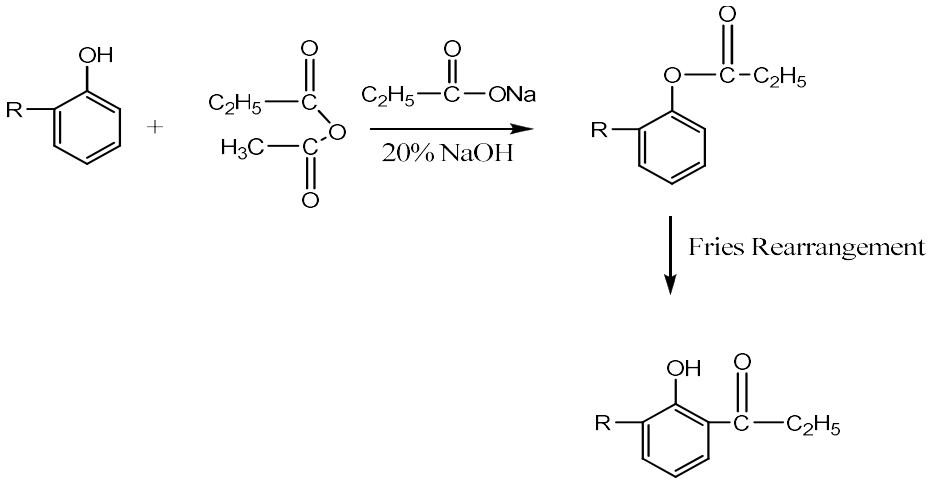
1. The first and foremost requirement is to have the through and exhaustive survey of related literature with focus on the targeted subject area / theme.
2. Design and development of synthetic route and optimization of synthetic conditions to achieve the desire Schiff base ligands derive from substituted hydroxypropiophenone with amine in alcoholic or suitable solvents medium . The formation Schiff base ligands will be confirmed by elemental and spectro-analytical data (IR, ^{1}H NMR, ^{13}C NMR and Mass).
3. Schiff base ligands will be reacted with metal salts in suitable solvents (DMSO/EtOH / MeOH) [Mn (II), Cr (III), Co (II), Ni (II), Cu (II), and Zn (II),] complexes will be obtained.
4. All prepared metal complexes will be characterized by elemental analysis, UV-Visible spectroscopy, IR, ^{1}HNMR, ^{13}CNMR, Mass, XRD, SEM and TGA/DTA analysis.
5. Magnetic susceptibility measurements of all complexes will be performed.
6. Molar conductance of all the synthesized complexes will be measured.
7. SEM and XRD analysis will be made to know the crystalline and surface morphological phase identification.
8. The Schiff base ligands and their complexes will be screened against bacteria and fungi.
9. Cu (II) complexes will be additionally characterized by ESR study .

Methodology to be adopted

We will adopt new synthetic methodology for the synthesis of Schiff bases and their metal complexes by using readily available starting material.

Preparation of substituted hydroxyl propiophenone:

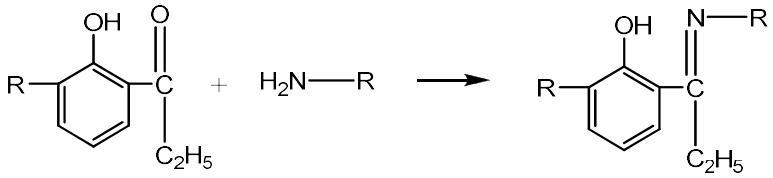
Synthesis of sub. hydroxypropiophenone would be accomplished by the reaction of Phenol/ sub. Phenol with propionic anhydride in the presence of sodium propionate to obtain phenyl propionate which on Fries rearrangement give sub. hydroxypropiophenone.



(a)

Preparation of Schiff bases:

The Schiff bases will be prepared by the condensation of substituted hydroxypropiophenone and aromatic or heterocyclic amines by refluxing in 1:1molar ratio in ethanol for 2 h. The product formed was separated by filtration, purified by re-crystallization from ethanol, washed with ethanol, and then dried.

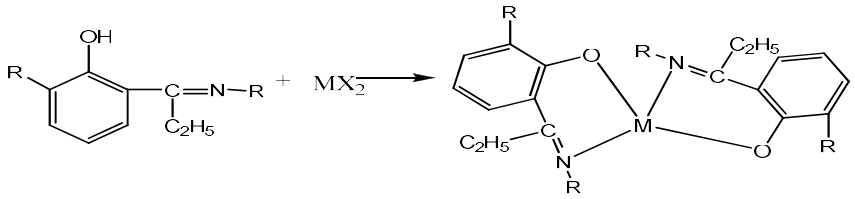


(b)

Synthesis of Metal Complexes:

The metal complexes will be prepared by adding the solution of the ligand in may use to ensure complete precipitation of the metal complexes.1 % KOH solution in methanol will be added to adjust the pH between7 to 8 and irradiated in Microwave oven for 2-10 min. Progress of the reaction was monitored on TLC.The precipitate so obtained was filtered washed and dried in vacuum

M = Cu, Cr, Ni, Co, Mn and Zn.



(c)

Importance of study

1. **International Status**:

The synthesized Schiff base and its metal complexes seem to be able to combine with the lipophilic layer in order to enhance the membrane permeability of the Gram-negative bacteria. The lipid membrane surrounding the cell favors the passage of only lipid soluble materials; thus the lipophilicity is an important factor that controls the antimicrobial activity. Also the increase in lipophilicity enhances the penetration of Schiff base and its metal complexes into the lipid membranes and thus restricts further growth of the organism (Tumer et al., 1999, Imran et al., 2007, Raman et al., 2009).

Schiff base and its metal complexes have been screened for their antimicrobial activities using the disc diffusion method against bacteria, the results of antimicrobial activity show that the metal complexes exhibit antimicrobial properties and they show enhanced inhibitory activity compared to the parent ligand under experimental conditions.

The antibacterial activity has been explained on the basis of chelation theory. Also, the results indicated that tested complexes were more active against Gram-positive than Gram-negative bacteria. It may be concluded that antibacterial activity of the compounds is related

to cell wall structure of the bacteria. It is possible because the cell wall is essential to the survival of many bacteria and some antibiotics are able to kill bacteria by inhibiting a step in the synthesis of peptidoglycan (El-Sherif and Eldebss, 2011)

2. **National Status:**

The metal complexes of Cu(II), Ni(II) and Co(II) with Schiff bases of 3-(2-hydroxy-3-ethoxybenzylideneamino)-5-methyl isoxazole and 3-(2-hydroxy-5-nitroben-zylidene amino)-5-methyl isoxazole which were obtained by the condensation of 3-amino-5-methyl isoxazole with substituted salicylaldehydes were screened against *Aspergillus niger* and *Rhizoctonia solani*. The ligands presented here and their transition metal complexes gave better results against the growth of fungi. It is found that the activity increases upon coordination. The increased activity of the metal chelates can be explained on the basis of chelation theory (Raman et al., 2001, Prashanthi et al., 2008). The orbital of each metal ion is made so as to overlap with the ligand orbital. Increased activity enhances the lipophilicity of complexes due to delocalization of pi-electrons in the chelate ring (Srivastava, 1981). In some cases increased lipophilicity leads to breakdown of the permeability barrier of the cell (Gupta et al., 1997, Cukurovali et al., 2002). The results of anti-fungal screening, indicate that Cu(II) complexes show more activity than the other complexes. These results may be due to higher stability constant of the Cu(II) complexes than the other complexes.

A Schiff base ligand derived from 1,4-dicarbonyl-phenyl-dihydrazide and chromene-2,3-dione (2:2) formed complexes with Cr(III), Mn(III), and Fe(III) metal salt in methanolic medium, then tested for their antimicrobial activities to assess their inhibiting potential. The antifungal experimental results of the compounds were compared with the standard antifungal drug (Miconazole) at the same concentration. All the metal complexes exhibited greater antifungal activity against *Aspergillus* sp. However, they show slightly lesser activity against *Rhizoctonia* sp. than standard drug Miconazole. The Cr(III) and Fe(III) complexes are more effective against *Penicillium* sp. than the standard drug. From the data it has been also observed that the activity depends upon the type of metal ion and varies in the following order of the metal ion: Cr > Fe > Mn (Kumar et al., 2012)

3. Significance:

Halo derivatives of Schiff bases are reported to have antimicrobial and antitumor activities. Antimicrobial and antifungal activities of various Schiff bases have also been reported. Some derivative of Schiff base & β- Lactam acts as good antimicrobial agents. Schiff base & metal complexes of Sulphur & nitrogen acts as good antibacterial agents. The crown ethers of Schiff bases are also examined to have a very good potential to act as anti-microbial agent. Some Schiff base Copper (II) complexes with phenanthroline and bipyridyl shows better antifungal activity to control the fungal diseases in human and plants. Thiazole containing Schiff's bases and their transition metal complexes were shown to be extensive range of biological activities. Considering the importance associated with these compounds they may be used as a future potential antimicrobial candidate in biological science.

Proposed Work Plan and Structure of the Study

First Year Plan:

First part of the research work will be the collection of literature in the relevant area to know the current status of Schiff bases both bidentate and tridentate ligands and corresponding transition metal complexes.

We will study basic concepts. Further, we may attend some international/national conferences and seminars to get acquainted deeply with the subject concerned in depth and also to get a broad understanding of the topic chosen from the experts Persons and Presenters in the field of the topic entitled for my research work.

By coupling all these data, I will come to a conclusion to implement different new methodologies for synthesis of Substituted hydroxypropiophenone. Substituted hydroxypropiophenone can be synthesized by using Fries migration method from substituted phenols.

Second Year Plan:

According to propose research plan, the reaction between hydroxypropiophenone and aromatic amines or heteroamines in alcoholic or suitable solvents medium yield Schiff base ligands . The progress of reaction will be monitored by TLC. Metal complexes will be prepared by following general method. An equimolar amount of ligand and respective metal salt[Cr (III), Mn (II), Co (II), Ni (II), Cu (II), and Zn (II),]will be dissolved separately in a suitable solvents . Both the solutions will be mixed in warm conditions with continuous stirring and reflux for suitable time to get products. Synthesized complexes will be analysed by elemental analysis and performing spectral analysis such as UV-Visible spectra, IR, ^{1}H NMR, ^{13}C NMR, Mass, XRD , SEM, TGA.The schematic route for the Schiff base ligands is shown as under:

We will refer references from conferences, seminars, workshops and internet and try to determine some new results. Results will be published in reputed Journals and may present data in seminars and conferences on the selected topic and publication of the same accordingly.

Third Year Plan:

Biological activities of all prepare complexes will be check against different bacterial strain by disc diffusion methodsduring second year plan. We will conclude the experimental results obtained and may submit for publications in standard journals during this year.
At the end of this year, we will plan for writing Ph. D. thesis work and submit same to Swami Ramanand Teerth Marathwada University, Nanded-431606, Maharashtra State, India for the Award of the Degree of Ph.D. in Chemistry.

Expected outcome of the proposed work

Schiff bases will be prepared by refluxing derivative of hydroxypropiophenone and aromatic amines or hetero amines in ethanol. Prepared Schiff base will combine with metal salts to form metal complexes. It is also expected that our studies on Schiff base compounds may throw some light on biological path and electronic effect of substituent's on ligands will provide better understanding of

Complexes may have good biological activity and hence they may be used as good drugs of choice to manage the bacterial and fungal diseases.Experience gained on executing this project and accomplished results will be presented in national conferences/workshops for promotion of this kind of research work and suggestions will be invited to improve the quality of research and better utilization of materials in science and technology of our country. Publication and patents may be outcome of this work. The outcome of the findings will be a contribution to the existing domain of the chemical sciences.

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